

RESEARCH HIGHLIGHT
Basic Sciences Program
Geosciences Subprogram

Project: Heterogeneous Nucleation and Growth Kinetics of Clays

Who and Where: Kathy Nagy and Randy Cygan

Geochemistry Department, Sandia National Laboratories,

Albuquerque, NM 87185-0750 (505-844-5337; FAX 844-7146)

Email: nagyk@spot.colorado.edu or rtcygan@sandia.gov

Objective: Clay nucleation and growth often occur heterogeneously and/or epitaxially on detrital minerals. Kinetics of these processes and role of nucleating substrates are unknown. The goal of the project is to quantify and model clay mineral growth by examining the reaction at the surface, to assess reactive surface area, and to provide kinetic data for accurate modeling of weathering and diagenesis.

Results: New data for gibbsite growth on powdered kaolinite and single crystal muscovite at 80°C in pH 3 solutions were combined with published data for gibbsite growth on gibbsite powders. All rates obey the same linear function of saturation state when reactive surface area is specifically considered. This function is $\text{Rate}_{\text{ppt}} = (2.6 \pm 0.3) \times 10^{-10} g^{(0.90 \pm 0.01)}$ where $g = \exp(-\Delta G_r^\ddagger / RT)$ and Rate_{ppt} has units of $\text{mol m}^{-2} \text{sec}^{-1}$. The equation applies for the measured range of saturation states from $\Delta G_r = 0$ to $2.1 \text{ kcal mol}^{-1}$, where $\Delta G_r = RT[\ln(Q/K)]$ for the reaction $\text{Al}^{3+} + 3\text{H}_2\text{O} = \text{Al}(\text{OH})_3 + 3\text{H}^+$, and equilibrium defined as $\Delta G_r = 0$ was previously determined. Identification of the growth phase as gibbsite was confirmed by rotating anode powder X-ray diffraction. Rates on kaolinite were determined using steady-state measured changes between inlet and outlet solutions in single-pass stirred-flow experiments. Rates on muscovite were determined by measuring the volume of precipitated crystals in images obtained by Tapping Mode™ atomic force microscopy (TMAFM). All rates were normalized to substrate surface area. Total BET surface areas were used for powdered gibbsite, ~ 8% of the BET surface area was used for powdered kaolinite, and the basal surface area imaged by TMAFM was used for single crystal muscovite. The kaolinite surface area represents the approximate edge area containing protonated aluminol sites. Linearity of growth rates with saturation state suggests that the dominant nucleation and growth mechanisms are two-dimensional. Such mechanisms are supported by observations of the morphologies of gibbsite crystals grown on muscovite at $\Delta G_r = 2.1 \text{ kcal mol}^{-1}$. The morphologies include (1) apparent epitaxial films as determined by hexagonal outlines of edges and thicknesses of 30 to 40 Å, (2) elongate crystals 30 to 40 Å thick aligned with the structure of the distorted Si-tetrahedral sheet of the 2M₁ muscovite, and (3) micron-scale three-dimensional clumps of intergrown crystals.

Significance: Reactive surface area for heterogeneous crystal growth in reactive-transport models must be modified to include substrates other than that of the growing mineral and to account for the role of geometric and chemical controls on epitaxial nucleation and growth.

Publication: A journal article entitled "Gibbsite growth kinetics on gibbsite, kaolinite, and muscovite substrates: AFM evidence for epitaxy and an assessment of reactive surface area" has been published in *Geochim. Cosmochim. Acta*, 16, 2337-2351, 1999.